# CONTROL OF THE CHEMICAL STATE OF GLASS SHEET SURFACE

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The leachability of sheet glass in time and across the ribbon width is investigated using different methods. It is demonstrated that the method for determining the thermal-emission capacity of the surface makes it possible to characterize the chemical resistance of glass.

One of the main parameters of the quality of glass is the ability of its surface to withstand the destructive effect of water, air moisture, and other chemical reactants. Since this parameter mainly depends on the alkali content in the surface layer and the state of the glass surface in the course of its production, storage, and service, leachability has been selected as the evaluation criterion. [1]. Leachability is the property of glass to emit a certain amount of alkali components via its surface into the ambient medium. The released alkali components later become bonded as sulfates of the alkali metal if leaching occurs in a sulfur dioxide atmosphere, or modify the plasma current under thermal treatment [2 – 4].

Considering sheet glass intended for construction, especially polished glass, whose chemical composition should guarantee its chemical resistance, numerous instances of surface destruction under the effect of the ambient moisture in storage and transportation indicate that the alkali content in the surface layers and the state of the sheet glass surface may vary substantially. Such variations depend on many factors, including technological ones. Therefore, a method is needed for systematic monitoring of the leachability of glass, which must be highly sensitive, fast, and reliable under industrial conditions.

Taking into account the disadvantages of the known methods, we have developed a method for the control of the leachability of glass by determining the parameters of thermal emission of alkali ions from the surface of silicate glass with an activated potential difference of 1200 V. The scheme of this setup is shown in Fig. 1.

A glass sample of size $12 \times 12 \times 3$ mm is placed on the lower electrode of the measurement cell. A graphite layer is deposited on the bottom surface of the sample for its better contact with the electrode surface. The positive pole of a direct current source is connected to the lower electrode and the negative pole is connected to the upper electrode. The up-

per electrode is installed at a height of 0.25 mm above the surface of the glass sample analyzed. The measuring cell is placed into the electric furnace of a DKV-4 quartz dilatometer, where the conditions needed for the thermal emission process are developed. The cold ends of the thermocouple are connected to a PDS two-coordinate potentiometer (axis $X$) and the strength of the emission current is recorded on the axis $Y$. On reaching a certain temperature, named hereafter the emission start temperature $t_{e.s}$, the surface starts emitting alkali ions.

The process of thermal emission was investigated at the heating rate of $4 – 6$ K/min (Fig. 2). The activated thermal emission curve is characterized by the emission start temperature and the angle $\beta$ of the rectilinear segment that determines the strength of the emission current depending on the glass surface temperature and the activation energy of the leaching process.

The physical meaning of the emission start temperature is characterizing the energy state of the surface alkali cation, which depends on its chemical environment. Special research demonstrated that $t_{e.s}$ primarily depends on the alkali content in glass. This is corroborated by the presence of a
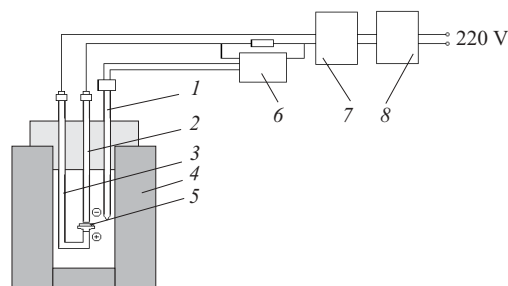


**Fig. 1.** Scheme for studying activated thermal emission processes: *1* ) thermocouple; *2* ) upper electrode; *3* ) lower electrode; *4* ) electric furnace; *5* ) glass sample; *6* ) two-coordinate potentiometer; *7* ) high-voltage source; *8* ) voltage stabilizer.

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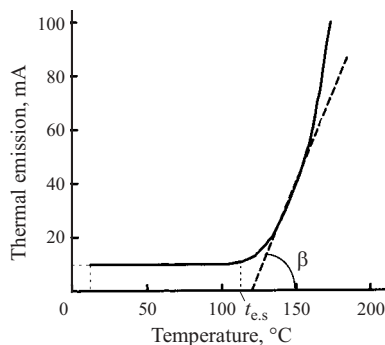[1] L'vovskaya Politekhnika National University, Lvov, Ukraine.

**Fig. 2.** Activated thermal emission curve.

correlation between $t_{e.s}$ and β (the correlation coefficient is equal to 0.99).

The study of a large number of samples selected from different sites of the glass ribbon at different times indicated that their $t_{e.s}$ lies within a range of 90 – 150°C. The confidence interval expressed as the mean quadratic error of the arithmetic mean for samples prepared from the same glass piece is ± 4.6°C with the confidence probability of 0.95.

In order to estimate the possibility of using $t_{e.s}$ as the criterion characterizing the alkali content of the glass surface, the chemical resistance of the same samples was performed using different methods. We analyzed samples of sheet glass BVVS cut out from the ribbon in the direction of its drawing. The samples were taken from the left and the right edges and the center of the ribbon after equal time spans for two months. Some samples from each sampling were analyzed immediately and the rest were placed in an exciccator filled with water to determine the dependence of $t_{e.s}$ on the state of hydrated glass surface.

In the first method the leachability was measured on plate-shaped samples with a total surface area of 100 cm$^2$. The samples were boiled for 5 h in distilled water with subsequent titration in 0.01 N HCl solution. Hereafter this method is called the MFS, i.e., the method of formation surfaces [5].

At the same time the water resistance of glass was measured by the granular method (GM) according to GOST 10134.1–82.

According to another method, the leachability was determined by the method of thermal emission (MTE).

Analysis of the results shown in Fig. 3 suggests the following conclusions.

The most significant variations (up to 45%) in chemical resistance with time and across the width of the glass ribbon width are typically registered with the granular method. This can be accounted for, on the one hand, by the imperfection of this method, and on the other hand, by using glass grains from the inner layers, which are known to differ significantly from the surface layers in their properties; therefore, the GM cannot objectively reflect the state of the glass surface regarding the alkali content.
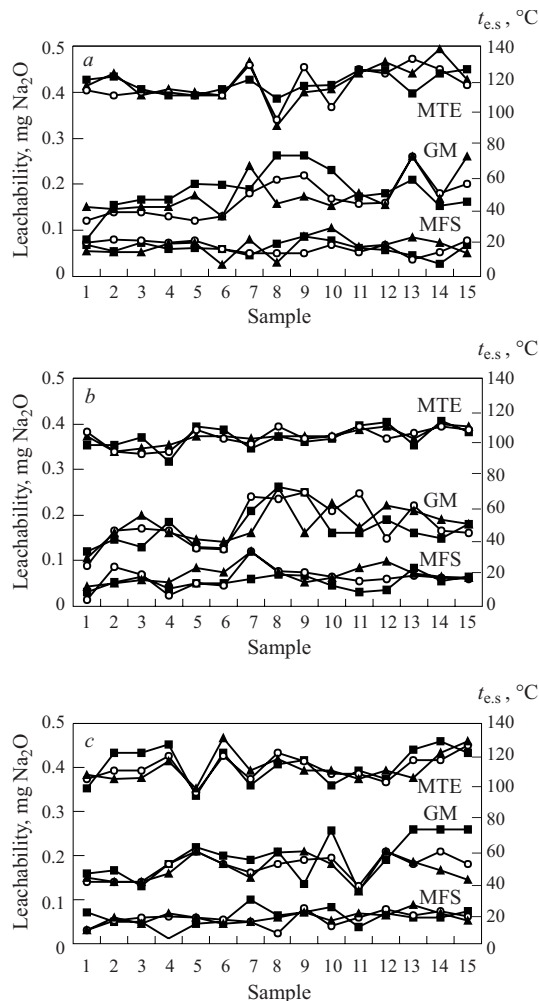


**Fig. 3.** Fluctuations in chemical resistance of sheet glass surface: *a*, *b*, and *c*) first, second, and third machine, respectively; ■) right edge; ○) center; ▲) left edge.

The MFS satisfies this requirement better. However, the use of large surface areas of the samples and the need to paraffinize their lateral surfaces make the method very complicated and decrease its accuracy [6].

The MTE demonstrates the relative stability of the alkali content in the glass surface across the ribbon width (deviations within 5%), although in certain time periods (Fig. 3*a*) such deviations can reach 15% or more (samples 7 – 10). At the same time, the alkali content in the glass surface layer is more stable on the second machine. The substantial fluctuations in $t_{e.s}$ recorded on the first machine are related to a break of the ribbon, and the time of reaching a stable operating regime according to the data in Fig. 3*a* is 5 days.

The highest instability in the period investigated was observed on the third machine; variations with time here reach 50%.

The lowest $t_{e.s}$ value is seen in samples 8, 4, and 5 (Fig. 3*a*, *b*, and *c*, respectively). When stored in a moist atmosphere, the specified samples had the worst state of the
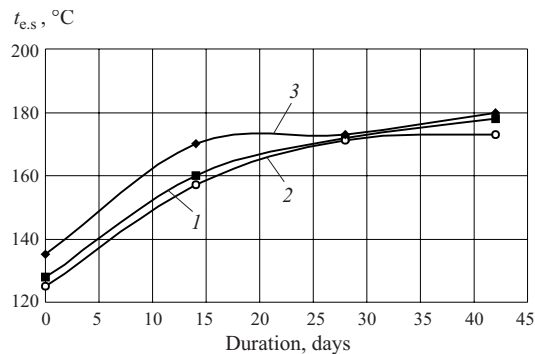
**Fig. 4.** "Self-deceleration" of destruction of glass by water: *1* ) right edge; *2* ) center; *3* ) left edge.

surface (emergence of corrosion). At the same time (according to the MFS data), the lowest chemical resistance was registered in samples 10, 7, and 7 (Fig. 3*a*, *b*, and *c*, respectively), which had no visual corrosion.

The MTE data on the state of the glass surface suggest that it is unadvisable to store glasses with a low $t_{e.s}$ in unfavorable conditions in view of their possible surface corrosion.

To verify the assumption that the emission start temperature objectively reflects the chemical state of the surface, the dependence of $t_{e.s}$ on the duration of storing the samples of the same sheet glass in a moist atmosphere was investigated. The obtained results support the theory of the "self-deceleration" of leachability due to the formation of a protective surface layer [7] (Fig. 4).

Thus, the proposed method for studying activated thermal emission of alkali ions from the glass surface makes it possible to estimate modifications occurring in the surface layers of glass based on the emission start temperature.

The use of the thermal emission method is especially promising for estimating the chemical state of the glass surface, as it can be implemented in a continuous operation directly on the systems for sheet glass production.

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